

UDC (679.823.2+666.192):532.614.2

## SURFACE ENERGY OF CRYSTALLINE AND VITREOUS SILICA

Yu. K. Shchipalov<sup>1</sup>Translated from *Steklo i Keramika*, No. 11, pp. 8–11, November, 2000.

A variant of evaluation of the theoretical values of the surface energy of quartz glass and various forms of crystalline silica based on analyses of the structures of these materials and experimental determination of the zeta-potential of  $\beta$ -quartz and amorphous silica is considered.

The surface energy of solids determines numerous properties of powders: the rate of dissolution in liquid media and melts, the rate of chemical reactions in heterogeneous systems, the sintering rate, the adsorption capacity of the powders (including hygroscopic adsorption), their tendency to cake, the specific heat of wetting, etc. Knowledge of the specific surface energy  $\sigma$  makes it possible to evaluate the energy spent on formation of interphase surfaces in milling. Therefore, in solving various theoretical and applied problems, much attention is given to aspects of experimental determination and calculation of  $\sigma$  for various materials.

There are several methods for determination of  $\sigma$  for solids, including crystalline and vitreous silica [1].

A drawback of methods based on determining the sorption capacity or the heat of wetting of the surface of a crystalline body by a liquid consists in lack of reliability of the juvenile purity of freshly fractured surfaces, accurate knowledge of the fracture surface relief, and accurate values of the interphase surface area. The method for evaluating  $\sigma$  for quartz glass by extrapolation of surface tension values for  $\text{SiO}_2$  melt at high temperatures (1300°C or more) and down to room temperature is not correct, since the surface tension of a melt is equal to the work done to form a unit of the melt surface by deformation without disturbing the liquid-medium continuity. The surface energy of a solid is equal to the work done to form a unit of its surface in destruction (disturbance of the medium continuity), i.e., the notions of surface tension and specific surface energy are not equivalent.

Methods for determining the parameter  $\sigma$  for amorphous (vitreous) silica based on surface tension data for glass melts extrapolated to the content of  $\text{R}_2\text{O}$  and RO in them equal to zero are even less correct.

R. Iler in his book [1] indicates  $\sigma$  for quartz equal to  $980 \times 10^{-3} \text{ J/m}^2$  ( $980 \text{ erg/cm}^2$ ).

It should be noted that experimentally obtained values of  $\sigma$  for quartz and quartz glass are affected by internal defects and impurities existing in the structure of the solids. Thus, the impurity content in very pure piez quartz and optical quartz glass can reach  $10^{-4} - 10^{-5} \%$ , or  $10^{-6} - 10^{-7}$  in fractions. In this case, the impurity content  $N_A$  is expressed by the enormous quantity  $6.02 \times 10^{23} \times 10^{-7} = 6.02 \times 10^{16}$  impurity particles per mole of silica (60 g).

At the same time, it is of interest to analyze and compare calculated (theoretical) values of  $\sigma$  for different silica modifications in the ideal variant (without impurities), which makes it possible to carry out a comparative evaluation of the surface properties of crystalline and vitreous  $\text{SiO}_2$ .

In the principal forms of  $\text{SiO}_2$ , each silicon atom is surrounded by four oxygen atoms, and each oxygen atom is surrounded by two silicon atoms. According to Poling, the degree of covalence of the Si–O bond constitutes 65% (according to other sources, it even reaches 80–89%). The length of the Si–O bond in different silica modifications varies from 0.158 (high-temperature cristobalite) to 0.166 nm or more, its mean value being 0.162 nm [2]. This value is taken as the basic value. In this case, the distance between the vertices of the silicon-oxygen tetrahedron (i.e., the distance between the oxygen atoms in it) constitutes 0.265 nm. The molar-energy values for the single bond  $E_{\text{Si-O}}$  vary as well for different modifications of  $\text{SiO}_2$ : 106, 102.8 ( $\alpha$ -cristobalite), and 102.25 (quartz glass) kcal/mole [2, 3].<sup>2</sup> We take  $E_{\text{Si-O}} = 106 \text{ kcal/mole} = 444 \text{ kJ/mole}$ .

Consequently, the single-bond energy in  $\text{SiO}_2$  is equal to:

$$\varepsilon_{\text{Si-O}} = E_{\text{Si-O}} / N_A = 444 / (6.02 \times 10^{23}) \text{ kJ/bond}.$$

When a solid is broken along some plane (*hkl*), two fracture surfaces with a certain number of lattice points that have broken bonds with the part of the crystal fractured off arise

<sup>1</sup> Ivanovo State Chemical Engineering University, Ivanovo, Russia.

<sup>2</sup> 1 kcal/mole = 4.1840 kJ/mole.

(their reticular density is  $d_{hkl}^{\text{ret}}$ ). If each of these lattice points has a certain number of broken (uncompensated) bonds ( $n^{\text{br}}$ ), it follows from the law of energy conservation that the specific surface energy of the solid is equal to

$$\sigma_{hkl} = \frac{1}{2} \varepsilon_{\text{Si-O}} d_{hkl}^{\text{ret}} n^{\text{br}}. \quad (1)$$

In the case of  $\text{SiO}_2$ , it is easiest to evaluate  $d_{hkl}^{\text{ret}}$  and  $n^{\text{br}}$  for the  $\alpha$ -cristoballite lattice, belonging to the cubic system (Fig. 1). The cell parameter  $a$  for this lattice is equal to 0.716 nm.

Theoretically, it is possible to compare the variants of  $\alpha$ -cristoballite crystal fracture along the planar networks  $\{001\}$  and  $\{111\}$ , although it is known that cleavage in  $\alpha$ -cristoballite (as in other forms of silica) is lacking or extremely unclear [4]. The fractures of all silica modifications usually have a conchoidal structure, but this does not prevent certain theoretical reasoning.

Assuming that  $\alpha$ -cristoballite breaks along the planar network  $\{001\}$ , one of the fracture surfaces will have only Si atoms with two broken bonds (known as a siliconized surface), while the other surface will contain twice as many O atoms with one broken bond (an oxylated surface). The surface area of an  $\alpha$ -cristoballite cell on the network  $\{001\}$  is  $a^2 = 0.716^2 = 0.5127 \text{ nm}^2$ . Statistically, there are two silicon atoms on this area (see Fig. 1) (one atom at the center of a cell face, and also  $4 \times 1/4$ , i.e., one, lattice point from the 4-vertex lattice points). The number of silicon atoms calculated per  $\text{nm}^2$  of  $\alpha$ -cristoballite fracture surface on the network  $\{001\}$  is equal to  $2 \times 1/0.5127 = 3.9$ , and the number of broken bonds is equal to  $3.9 \times 2 = 7.8$ . Then,

$$\sigma_{001} = \frac{1}{2} \varepsilon_{\text{Si-O}} \times 3.9 \times 2 = 3.9 \varepsilon_{\text{Si-O}} \text{ per nm}^2. \quad (2)$$

The quantity  $\sigma_{001}$  for oxylated surfaces will be the same, assuming that the energy of the single bond  $\varepsilon_{\text{Si-O}}$  is equally distributed between the two surfaces of  $\alpha$ -cristoballite fracture.

Figure 2 shows the structure of  $\alpha$ -cristoballite projected on the plane  $\{111\}$ . The structure can be represented as a three-dimensional skeletal chain of silicon-oxygen tetrahedra  $[\text{SiO}_4]$  that are helically joined to each other. These tetrahedra in the lattice structure are located at different levels. The vertices of tetrahedra  $[\text{SiO}_4]$  of the first level 1 are directed upward: these are broken Si-O bonds. To preserve the electrical neutrality of the fracture surface, these vertices are alternately electropositive ( $\equiv\text{Si}-\text{O}^+$ ) and electronegative ( $\equiv\text{Si}-\text{O}^-$ ). The vertices of tetrahedra  $[\text{SiO}_4]$  of type 2 located below the indicated level are directed downward, and these tetrahedra are linked to tetrahedra of a lower level 3, etc. (3 linked to 4, 4 to 5, 5 to 6). It can be seen that in the case of a perfect fracture of  $\alpha$ -cristoballite along the plane

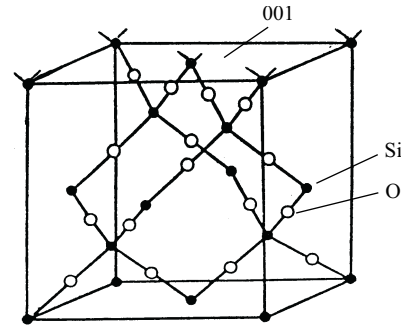


Fig. 1. Elementary cell of  $\alpha$ -cristoballite.

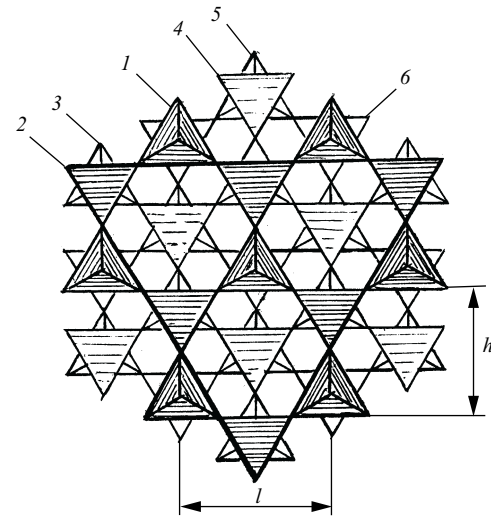


Fig. 2. Projection of the  $\alpha$ -cristoballite structure on the plane  $\{111\}$ .

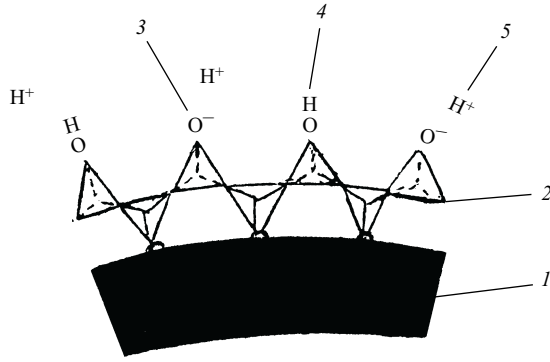
$\{111\}$ , broken bonds will be observed only in tetrahedra of type 1 (one bond per tetrahedron), i.e., not all points of the  $\text{SiO}_2$  lattice located on the fracture surface will have uncompensated bonds (in the perfect case).

It is possible to distinguish an elementary loop of area  $l \times h$  on the fracture surface  $\{111\}$ , and it is easy to calculate that there is one broken Si-O bond per elementary loop (half a bond each from two tetrahedra of type 1). These loops completely fill the fracture surface and form a pattern similar to brickwork, with a loop shift of  $\frac{1}{2} l$ . The quantity  $l$  is

equal to the sum of two edges of a tetrahedron ( $2 \times 0.265 = 0.53 \text{ nm}$ ). The loop height  $h = 2 \times 0.265 \sin 60^\circ = 0.458 \text{ nm}$ , and its surface area  $l \times h = 0.530 \times 0.458 = 0.2438 \text{ nm}^2$ . The number of lattice points with uncompensated bonds calculated per  $\text{nm}^2$  of the network  $\{111\}$  will be equal to  $1 \times 1/0.2438 = 4.1$ , and

$$\sigma_{111} = \frac{1}{2} \varepsilon_{\text{Si-O}} \times 4.1 = 2.05 \varepsilon_{\text{Si-O}} \text{ per nm}^2. \quad (3)$$

A comparison of expressions (2) and (3) shows that the energy spent on breaking  $\alpha$ -cristoballite along the network



**Fig. 3.** Model of a hydroxylated surface of silica: 1) micelle nucleus; 2) surface film of silicic acid; 3) potential-determining ions; 4 and 5) adsorption and diffusion counterion layers, respectively.

{001} is almost double the energy spent on fracture along the network {111}. This means that the second variant of fracture is highly preferable. Obviously, the presence of real defects and impurities in cristobalite (and in  $\beta$ -quartz and quartz glass) dramatically alters the character of the fracture surface (which is conchoidal rather than flat); however, the tendency to have a certain portion of the tetrahedra  $[\text{SiO}_4]$  with one uncompensated bond on this surface is retained.

The following argument can be offered to support this point of view. When  $\text{SiO}_2$  breaks along the plane {111}, the fracture surface is electrically neutral. In the case of a break along the plane {001}, the oxylated surface will be electronegative and the siliconized surface will be electropositive. Since the electronegativity of Si and O is, respectively, 1.9 and 3.6 [5], the specific surface energy of the oxylated fracture surface  $\sigma_{001}^{\text{O}^-}$  is actually twice that of the siliconized surface  $\sigma_{001}^{\text{Si}^+}$ , i.e., one surface receives  $2/3\varepsilon_{\text{Si-O}}$  from each broken Si-O bond, and the other surface gets  $1/3\varepsilon_{\text{Si-O}}$ , and not  $1/2\varepsilon_{\text{Si-O}}$  to each surface, as occurs in the simplified variant. A substantial difference in the specific surface energies  $\Delta\sigma_{001}$  is observed between the indicated surfaces (an affinity of the fracture surfaces), a consequence of which is strong cohesion and restoration of the lattice.

Considering that  $\varepsilon_{\text{Si-O}} = 444/(6.02 \times 10^{23})$  kJ/bond,  $1 \text{ kJ} = 10^3 \text{ J}$ ,  $1 \text{ J} = 10^7 \text{ erg}$ , and  $1 \text{ cm}^2 = 10^{14} \text{ nm}^2$ , we obtain for  $\alpha$ -cristoballite:

$$\begin{aligned}\sigma_{001}^{\text{av}} &= \frac{444 \times 10^3 \times 10^7 \times 10^{14}}{2 \times 6.02 \times 10^{23}} \times 7.8 = \\ &2875.32 \text{ erg/cm}^2 \approx 2.875 \text{ J/m}^2; \\ \sigma_{111} &= \frac{444 \times 10^3 \times 10^7 \times 10^{14}}{2 \times 6.02 \times 10^{23}} \times 4.1 = \\ &1511.38 \text{ erg/cm}^2 \approx 1.511 \text{ J/m}^2.\end{aligned}$$

It is of interest to note that the calculated values of  $\sigma$  for the diamond lattice are  $\sigma_{111} = 5620 \text{ erg/cm}^2$  and  $\sigma_{001} = 3820 \text{ erg/cm}^2$  [6]. It can be seen that for these materials  $\sigma$  has a certain correlation with the Mohs hardness (10 for dia-

mond and 7 for  $\text{SiO}_2$ ). It is known that the hardness as well is determined by the quantity  $\varepsilon$ .

Knowing the density  $\rho$  of  $\alpha$ - and  $\beta$ -cristoballite (2.20 and 2.32 g/cm<sup>3</sup>),  $\beta$ -quartz (2.65 g/cm<sup>3</sup>), and quartz glass (2.20 g/cm<sup>3</sup>), it is easy to evaluate the number of mechanically broken bonds per unit surface area (1 nm<sup>2</sup>) for these materials:

$$n_{\beta\text{-cr}} = \frac{n_{\alpha\text{-cr}}}{(\rho_{\alpha\text{-cr}} / \rho_{\beta\text{-cr}})^{2/3}} = \frac{4.1}{(2.20 / 2.32)^{2/3}} = 4.25;$$

$$n_{\beta\text{-q}} = \frac{n_{\beta\text{-cr}}}{(\rho_{\beta\text{-cr}} / \rho_{\beta\text{-q}})^{2/3}} = \frac{4.25}{(2.32 / 2.65)^{2/3}} = 4.63;$$

$$n_{\text{q.g}} = \frac{n_{\beta\text{-cr}}}{(\rho_{\beta\text{-cr}} / \rho_{\text{q.g}})^{2/3}} = \frac{4.25}{(2.32 / 2.20)^{2/3}} = 4.13.$$

By substituting the obtained values of  $n$  into the formula  $\sigma = 1/2\varepsilon_{\text{Si-O}} n$ , we get

$$\sigma_{\beta\text{-cr}} = 1566.68 \text{ erg/cm}^2 \approx 1.567 \text{ J/m}^2;$$

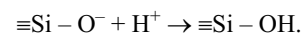
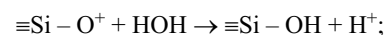
$$\sigma_{\beta\text{-q}} = 1706.75 \text{ erg/cm}^2 \approx 1.707 \text{ J/m}^2;$$

$$\sigma_{\text{q.g}} = 1522.45 \text{ erg/cm}^2 \approx 1.522 \text{ J/m}^2.$$

Apparently, the coincidence of the calculated values of  $\sigma$  for  $\alpha$ -cristoballite and quartz glass (1.511 and 1.522 J/m<sup>2</sup>, respectively) should be indubitable, since their densities are equal. However, the actual situation is more complicated.

Determination of the electrokinetic potential  $\xi$  of fine (1–30  $\mu\text{m}$ ) particles of pure  $\beta$ -quartz and quartz glass held in doubly distilled water for 4–5 days, using the microelectrophoresis method, showed that the  $\xi$ -potential of particles of hydrated  $\beta$ -quartz (–42 mV) is lower than that of particles of hydrated quartz glass (–45 mV), i.e., the actual electrical-surface activity of quartz glass in water is 1.07-fold higher than that of  $\beta$ -quartz.

At the same time, in hydroxylation of surface lattice points of these materials, the active centers are primarily sites with broken (uncompensated) Si-O chemical bonds (i.e.,  $\equiv\text{Si}-\text{O}^+$  and  $\equiv\text{Si}-\text{O}^-$ ). Presumably the surface of hydrated silica particles (micelles) to a great extent inherits the type of fracture surface observed in pure silica modifications. Silicon-oxygen tetrahedra with their vertices alternately directed upward (toward the dispersion medium) and downward (toward a micelle nucleus) are located on the hydrated fracture surface (Fig. 3). Due to reaction with water molecules vertices oriented toward the liquid transform into OH groups, which arise according to the following scheme:



Two other vertices of  $[\text{SiO}_4]$  tetrahedra are directed toward the viewer and into the plane of the figure, ensuring the

presence of a continuous surface film of silicic acid of composition  $\text{H}_2\text{Si}_4\text{O}_9$  enveloping the micelle. Partial dissociation of this acid leads to the appearance of a negative surface charge on the micelles (potential-forming  $\text{O}^-$  particles) and a  $\xi$ -potential at the gliding interface.

The hydrogen particles contained in nondissociated OH groups form an adsorption counterion layer, and the protons  $\text{H}^+$  arising in the dissociation of OH groups form a diffusion layer.

The higher  $\xi$ -potential of hydrated quartz glass particles ( $-45$  mV) compared to that of  $\beta$ -quartz particles ( $-42$  mV) is the evidence of a larger number of OH groups per unit surface area of the micelles in glass (and, consequently, a larger number of ruptured Si – O – Si bonds per unit surface area of quartz glass) compared to the surface of  $\beta$ -quartz, i.e.,  $n_{\text{q.g}}^{\text{actual}} > n_{\beta\text{-q}}$ . It is obvious that  $n_{\text{q.g}}^{\text{actual}}/n_{\beta\text{-q}} = \xi_{\text{q.g}}/\xi_{\beta\text{-q}}$ , whence

$$n_{\text{q.g}}^{\text{actual}} = n_{\beta\text{-q}} \frac{\xi_{\text{q.g}}}{\xi_{\beta\text{-q}}} = 4.63 \times \left( \frac{-45}{-42} \right) = 4.95 \text{ per nm}^2.$$

In the same way:

$$\sigma_{\text{q.g}}^{\text{actual}} = \sigma_{\beta\text{-q}} \frac{\xi_{\text{q.g}}}{\xi_{\beta\text{-q}}} = 1707 \times \left( \frac{-45}{-42} \right) = 1824.71 \text{ erg/cm}^2 = 1.825 \text{ J/m}^2.$$

The difference  $n_{\text{q.g}}^{\text{actual}} - n_{\text{q.g}}^{\text{calc}} = 4.95 - 4.13 = 0.82 \text{ bond/nm}^2$  correlates with the number of thermally broken bonds per unit surface area of quartz glass particles. Indeed, in producing  $\text{SiO}_2$  melt at high temperatures ( $2000^\circ\text{C}$  or more), a substantial number of Si – O – Si bonds are thermally broken, which is accompanied by uncoupling of electrons in  $sp^3$  valence orbitals of Si atoms and  $p$  orbitals of O atoms. In the case of rapid cooling of the melt, these orbitals do not have time to overlap each other, and the thermal ruptures of Si – O – Si bonds become “frozen.” An example of such a rupture in Fig. 2 can be rupture of the bond between tetrahedra of types 1 and 2 along the bridge oxygen atom (the common vertex). Such breaks impart a certain looseness to the quartz glass structure (a kind of nonequilibrium internal defect), which is one of the most important reasons for its thermodynamic instability. The same reason explains why the energy consumed on formation of unit interphase surface in

quartz glass ( $\sigma_{\text{q.g}}^{\text{calc}} = 1.522 \text{ J/nm}^2$ ) is lower than in  $\beta$ -quartz ( $\sigma_{\beta\text{-q}} = 1.707 \text{ J/nm}^2$ ), while the overall of surface energy level, on the other hand, is higher in quartz glass ( $\sigma_{\text{q.g}}^{\text{actual}} = 1.825 \text{ J/m}^2$ ). Quartz glass arrives at the milling stage with a substantial number of Si – O – Si bonds in its structure already thermally broken (inheritance from the melt), which is not the case in  $\beta$ -quartz.

The present paper introduces certain corrections to the values of  $n$  for  $\beta$ -quartz and quartz glass quoted in [7]. The reasoning in the latter publication was based on the number of broken bonds per  $\text{nm}^2$  of cristobalite surface equal to 4.6, which was taken from R. Iler's book [1]. A more detailed analysis of the  $\alpha$ -cristobalite lattice indicated that for this material  $n = 4.1$ , and  $n = 4.6$  should refer to  $\beta$ -quartz. The value  $n_{\text{q.g}}^{\text{actual}} = 5.37$  for quartz glass was given in [7], although this parameter most likely is 4.95, and the number of thermally broken bonds per  $\text{nm}^2$  of quartz glass surface area is equal to 0.82 rather than 0.9. However, these discrepancies do not disprove the fundamental approach to the calculation of theoretical values of specific surface energy for crystalline and vitreous silica.

Experimentally found quantities  $\sigma$  frequently have values that do not coincide with theoretical-calculation data and even significantly differ among themselves, due to the complexity of the experiment, lack of guarantee of the juvenile purity of freshly formed interphase surfaces, the impossibility of total exclusion of gas adsorption on these surfaces, and the effect of impurities contained in the silica (even in very small quantities).

## REFERENCES

1. R. Iler, *Chemistry of Silica*, Wiley, New York (1979).
2. V. P. Pryanishnikov, *The Silica System* [in Russian], Stroiizdat, Leningrad (1971).
3. R. L. Muller, “Chemistry of solids and the vitreous state,” in: *Chemistry of Solids* [Russian translation], Leningrad (1965), pp. 9 – 63.
4. J. Dana, E. Dana, et al., *The System of Mineralogy, Vol. 3. Silica Minerals*, New York (1962).
5. S. S. Batsanov, *Electronegativity of the Elements and the Chemical Bond* [in Russian], Novosibirsk (1962).
6. A. Adamson, *The Physical Chemistry of Surfaces*, Wiley, New York (1976).
7. Yu. K. Shchepalov, “Evaluation of electrical-surface properties of particles of hydrated quartz glass based on the value of the zeta-potential,” *Steklo Keram.*, No. 11, 3 – 6 (1999).